(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 342 169 A3**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 89830205.4

(22) Date of filing: 10.05.89

(51) Int. Cl.5: B01D 53/36, C02F 1/78

(30) Priority: 11.05.88 JP 114388/88

(43) Date of publication of application: 15.11.89 Bulletin 89/46

(84) Designated Contracting States: DE FR GB IT

(88) Date of deferred publication of the search report: 11.04.90 Bulletin 90/15

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(54) **Electrolytic ozonizer and method of decomposing ozone-containing waste gas using said ozonizer.**

(57) The present invention is directed toward an electrolytic ozonier for treating ozone-containing waste gas and a method of treating ozone-containing waste gas using the ozonier, wherein the method includes evolving oxygen and ozone in an anode compartment of an electrolytic cell by electrolysis of water while evolving hydrogen in a cathode compartment; directing the evolved hydrogen into a waste gas treating section that contains a waste gas decomposition catalyst so as to convert the hydrogen to a harmless form by means of the catalyst; bringing the oxygen and ozone into contact with a medium to be treated in an ozone contactor so as to treat the medium; and subsequently directing waste gas containing oxygen and ozone produced as a result of treatment of the medium into the waste gas treating section where they are brought into either direct or indirect contact with the catalyst so that the ozone in the waste gas is converted into a harmless form.

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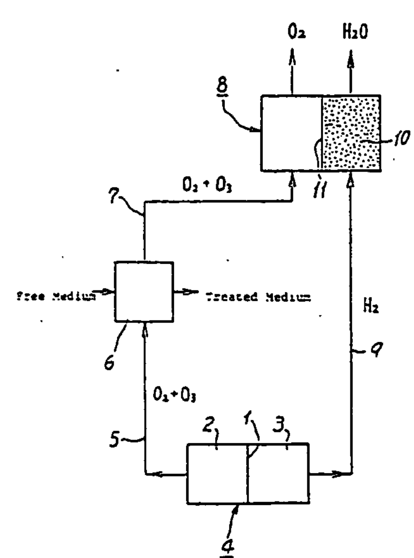
FIG. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 83 0205

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
E	US-A-4 836 929 (H. BAUMANN) * Whole document * ---	1,3,4,5	B 01 D 53/36 C 02 F 1/78
P,X	EP-A-0 281 940 (B.B.C. BROWN BOVERI AG) * Whole document * -----	1,3,4,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 02 F B 01 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-01-1989	PYFFEROEN K.

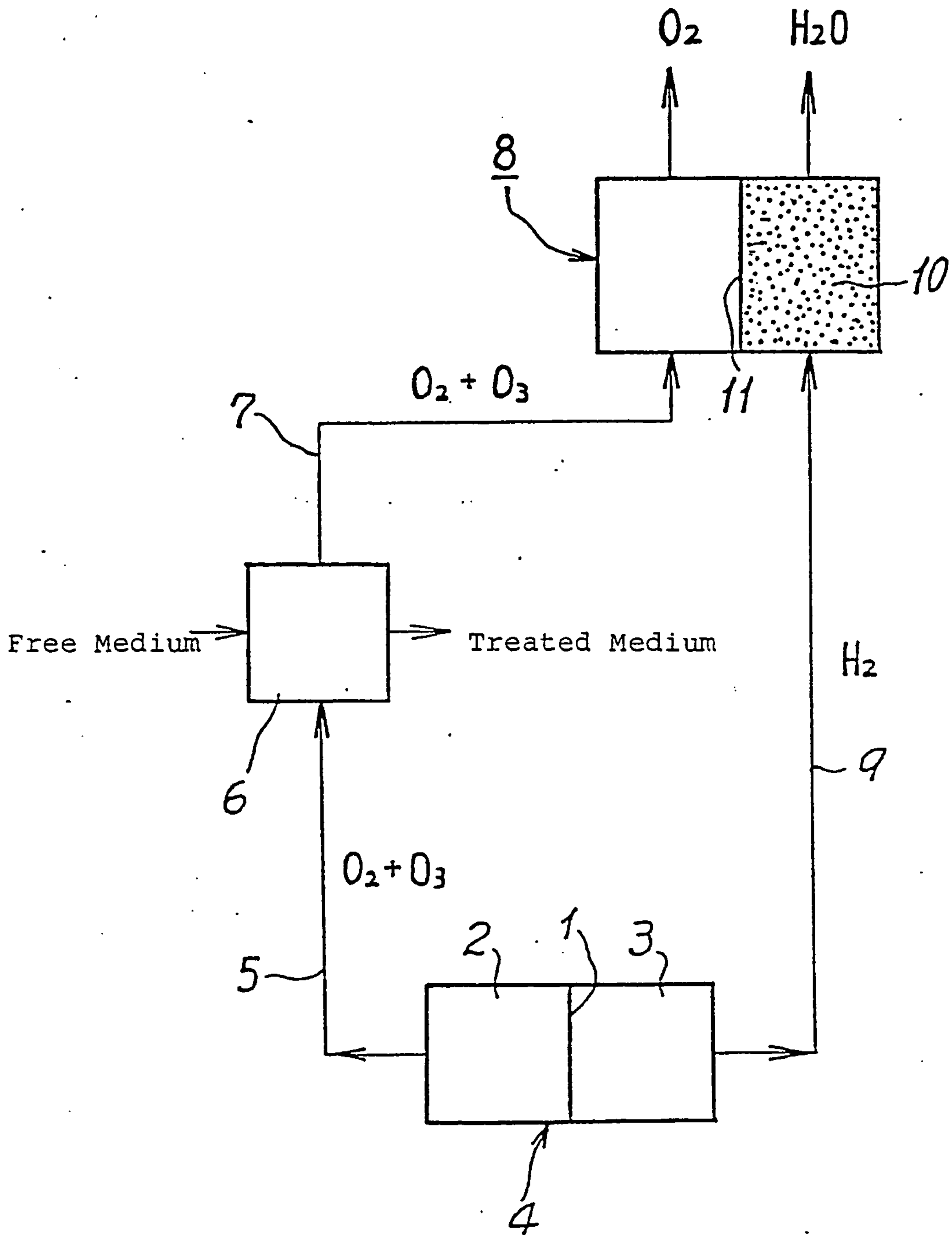
CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

F I G. 1


O2
H2O
8
10
11
O2 + O3
7
Free Medium
Treated Medium
H2
6
9
O2+O3
2
1
3
5
4

Nickel, palladium, platinum or various other conventional materials may be used as the hydrogen conversion (combustion) catalyst in the present invention and a suitable catalyst may be selected in accordance with the specific type of equipment and operating conditions. A palladium-based catalyst is preferred since it does not require any special treatment such as heating.

The shape and structure of the waste gas decomposing section are not limited in any particular way as long as one of the following requirements is met: the hydrogen gas introduced makes contact with the hydrogen conversion catalyst in it so that it is converted to water vapor, and the heat generated upon this conversion allows the ozone in the simultaneously introduced ozone-containing waste gas to be nearly completely converted to oxygen gas; or a alternatively, the ozone-containing waste gas introduced makes contact with the hydrogen conversion catalyst and reacts with hydrogen to be converted to water. An example of the waste gas decomposing section is shown in Fig. 2; the hydrogen conversion catalyst 10 is packed in a cylinder 12, into which a pair of conduit 7 and 9 are partly inserted from the bottom, with ozone-containing waste gas being supplied through the conduit 7 and hydrogen gas through the conduit 9. Hydrogen, ozone and oxygen are reacted in the cylinder 12 to form water vapor, which is released into air atmosphere through a discharge pipe 13 extending from the top of the cylinder 12. Instead of being inserted into the cylinder 12, the conduits 7 and 9 may be connected to the bottom of the cylinder in such a way that ozone-containing waste gas will mix with hydrogen gas before they get into the cylinder 12. In this case, in order to avoid the explosion hazard of mixing the two gases, they are desirably mixed in an area that is as close as possible to the cylinder 12.

Another example of the waste gas decomposing section is shown in Fig. 3. The hydrogen conversion catalyst 10 is packed in a cylinder 12, into which a conduit 9 for hydrogen gas is partly inserted from the bottom. A conduit 14 for ozone-containing waste gas penetrates transversely through the middle of the cylinder 12. In this embodiment, ozone-containing waste gas makes indirect contact with the catalyst 10 via the wall of the conduit 14 and the heat generated by combustion of hydrogen gas allows the ozone in the ozone-containing waste gas to be converted to oxygen. The outer surfaces of the conduits that contact the catalyst 10 are preferably clad with copper or a copper alloy. In another example of the waste gas decomposing section, the conduit for ozone-containing waste gas may be wound helically around the portion which is filled with the hydrogen conversion catalyst.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

EXAMPLE 1

An electrolytic cell for an electrolytic ozonizer was fabricated using the following components: an anode current collector in the form of titanium mesh; a cathode current collector in the form of nickel mesh; a solid polymer electrolyte (Nafion 117) coated on one side with a paste prepared by mixing a lead oxide (i.e., an anode catalyst having high ozone generating ability) and an aqueous polytetrafluoroethylene (PTFE) suspension (30J), and on the other side with a paste prepared by mixing a platinum powder (i.e., a cathode catalyst) and an aqueous PTFE suspension (30J), said electrolyte being rolled into sheet form at a pressure of 100 kg/cm^2 and at a temperature of 100°C; and a titanium anode and a SUS 304 cathode, each having an area of 45 cm^2. These components were assembled into the electrolytic cell. When ion-exchanged water supplied into the anode compartment was electrolyzed with a current of 45A being applied (density, 100 A/dm^2), wet oxygen gas containing 15 wt% ozone was evolved at the anode at a rate of about 9 ℓ/h (equivalent to ozone generation of about 2 g/h). Wet hydrogen gas was evolved at the cathode at a rate of about 19 ℓ/h.

The evolved hydrogen gas was introduced into a cylinder in mesh form (capacity, 30 mℓ) containing 25 g of a combustion catalyst that had 0.5 wt% palladium supported on 3-mmφ alumina particles having specific surface areas of 200 to 300 m^2/g. The temperature measured at the hydrogen exit of the cylinder was as high as 380° C whereas the temperature around the cylinder was 200°C.

The gaseous mixture of ozone and oxygen which was evolved in the anode compartment was introduced through a glass filter (0.5 μm) into a tank of municipal water, where tiny bubbles of the mixed gas were brought into contact with the municipal water to form ozonized water. Ninety-five percent of ozone in the mixed gas was absorbed and dissolved in the municipal water whereas 5% of ozone remained in the vapor phase. The concentration of residual ozone was equivalent to 5,000 ppm.

The resulting ozone-containing waste gas was introduced into a copper clad titanium pipe in the catalyst-filled cylinder of the type shown in Fig 2. The titanium pipe had a diameter of 10 mm, with the copper cladding being 1 mm thick. After contact for 3 seconds, the concentration of ozone at the exit of the cylinder dropped to 0.1 ppm and below.

EXAMPLE 2

Municipal water was ozonized and the resulting ozone-containing waste gas was treated using the same apparatus as what was employed in Example 1 except that the combustion catalyst-filled cylinder was replaced by the type shown in Fig. 3. The concentration of ozone in the effluent waste gas was 0.1 ppm; the temperature in the central portion of the cylinder was 360°C; and the contact time was 3 seconds.

In the electrolytic ozonizer of the present invention, water is electrolyzed in an electrolytic cell and the gaseous mixture of ozone and oxygen that is evolved in the anode compartment is used to treat a m dium such as water. The resulting ozone-contain-

Description

ELECTROLYTIC OZONIZER AND METHOD OF DECOMPOSING OZONE-CONTAINING WASTE GAS USING SAID OZONIZER

FIELD OF THE INVENTION

The present invention relates to an electrolytic ozonizer for treating ozone-containing waste gas, as well as a method of treating ozone-containing waste gas using said ozonizer.

BACKGROUND OF THE INVENTION

Because of its strong oxidizing power, ozone is extensively used in the treatment of water and air. In particular, ozone is used in the decomposition of organic matter. Commercial methods used today to produce ozone, include the corona discharge of air or oxygen, the electrolysis of water, and the irradiation of air or oxygen with UV light having a specified wavelength.

The corona discharge method was commercialized first since it can be operated with simple equipment and the electric power requirements for production are small. This method is primarily used to disinfect municipal water where large quantities of ozone are needed. However, in order to ensure efficient discharge, the feed gas must be completely dried, and oxygen gas must be used to increase the concentration of the ozone product. The discharge method, therefore, has the drawback that it requires complex facilities to be used in conjunction with the discharge unit. Another problem with the discharge method is that if air is used as the feed gas, noxious gases such NOx will be generated and the fine particulates formed as a result of the consumption of the discharge electrodes will substantially effect the purity of the ozone product.

The irradiation of air or oxygen with ultraviolet rays is incapable of producing ozone in high concentrations.

The electrolytic method uses only pure water as the liquid electrolyte and is capable of producing impurity-free ozone at high concentrations of 10 - 15% by electrolysis. Since the electric power requirements of this method are several times as large as those of the discharge method, its use is limited to small-scale equipment which can be operated at comparatively low cost or power.

In the methods of ozone generation described above, use of the generated ozone product in the treatment of water or air is generally no more than about 90% efficient. Thus, it is necessary to treat the waste gas containing unused ozone.

In an electrolytic ozone generator as described in U.S. Patent 4,416,747, a gaseous mixture of ozone and oxygen is evolved at the anode while at the same tim , hydrogen gas is evolved at the cathode. Therefore, one of the great problems with this type of ozone generator is how to deal with the ozone-containing waste gas and hydrogen gas that remain after the treatment of a medium. Conventionally, the hydrogen gas is converted to water vapor by combustion with the aid of a hydrogen burning catalyst, whereas the ozone-containing waste gas is separately converted to oxygen with the aid of an ozone decomposition catalyst. These catalysts render the waste gases entirely harmless. However, the ozonizer itself is bulky and requires cumbersome operations.

SUMMARY OF THE INVENTION

The present invention solves the aforementioned problems occuring with the use conventional electrolytic methods of ozone generation. Namely, the present invention solves the problems of increased equipment size and complexity of operations due to the need to perform separate treatments on ozone-containing waste gas and hydrogen gas using two different kinds of catalysts.

An object, therefore, of the present invention is to provide an electrolytic ozonizer that is simpler in structure and that is capable of more efficient treatment of waste gases.

Another object of the present invention is to provide a method of treating waste gases using said ozonizer.

The first object of the present invention is attained by an electrolytic ozonizer comprising an electrolytic cell in which oxygen and ozone are evolved in an anode compartment by electrolysis of water, and hydrogen is evolved in a cathode compartment, said anode compartment being connected to a waste gas decomposing section that accommodates a waste gas decomposition catalyst, with a medium treating ozone contactor being interposed between said anode compartment and said waste gas decomposing section, and said cathode compartment being connected to said waste gas decomposing section, with the ozone-containing waste gas which is produced as a result of treatment of said medium in said ozone contactor and said hydrogen gas evolved in the cathode compartment being brought into either direct or indirect contact with said catalyst to be converted to a harmless form.

The second object of the present invention is attained by a method of treating waste gases which comprises: evolving oxygen and ozone in an anode compartment of an electrolytic cell by electrolysis of water while evolving hydrogen in a cathode compartment; directing the evolved hydrogen into a waste gas treating section that accommodates a waste gas decomposition catalyst so as to convert said hydrogen to a harmless form by means of said catalyst; bringing said oxygen and ozone into contact with a medium to be treated in an ozone contactor so as to treat said medium; and subsequently directing waste gas containing oxygen and ozone produed as a result of treatement of said